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Ballistic Missile Defense Organization

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**Development of Quantum Dot Materials for Optical Devices
by the Sol-Gel Method**

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ABSTRACT

This Final Technical Report presents a summary of the research conducted from June, 1994 to January, 1998 on the development of semiconductor quantum dot materials prepared by a sol-gel method. The process involved the preparation of a sol-gel liquid solution with a chemical composition corresponding to that of a sodium borosilicate glass, the addition of a cadmium salt to the solution, the formation of a porous gel, the conversion of the cadmium salt to CdS and the densification of the gel into a glass at around 500°C. By systematic variation of processing conditions CdS quantum dots (QD) of uniform size and size distribution were prepared. For the first time, optical gains were achieved at room temperature. By ion-exchange of K for Na, waveguides were fabricated. The CdS particles were shown to be single crystals of about 40Å in dimension. Techniques were developed to prepare CdTe and PbS QD's in sodium borosilicate glass. Not only are the Bohr radii of PbS and CdTe much larger than that of CdS, which will give more efficient QD's samples, but the beginning of a systematic study of these three semiconductors would shed light on the presently unknown effects of the relatively large surface areas of QD's. A search of the literature revealed that the semiconductor SbSI is also a ferroelectric. It is theorized that an electric field induced dipole in SbSI would act to pin down the exciton created by a laser beam. Thus, longer lifetimes of the electron-hole pair are possible. Preliminary work has resulted in the successful preparation of SbSI QD's in the same sodium borosilicate glass. Verification of the behavior of SbSI now awaits further research.

1. Introduction and Background

In the past three and one-half years, active collaborations between Professor J.D. Mackenzie's group at UCLA And Professor N. Peyghambarian's group at the University of Arizona on semiconductor quantum dot materials and device development have continued. At UCLA, quantum dot materials based on CdS crystallites in different matrices were prepared and characterized. A new method was developed which enabled the successful preparation of samples with a very narrow size-distribution of CdS crystallites. Different types of samples were sent to Arizona for testing and device development. The characterization work at the University of Arizona revealed that the new samples have higher $\chi^{(3)}$ values and did not exhibit photodarkening, as the common melt-derived glasses do. This collaboration has resulted in the fabrication of the first quantum dot channel waveguide. The waveguide device was fabricated by ion exchange and etching procedures. Initial pulse propagation experiments (that were performed in Arizona) in these waveguides are extremely interesting, verifying that the waveguides are of high optical quality and showing pulse breakup effects. It was therefore proposed that this fruitful collaboration between the two groups be continued. UCLA would be responsible for the preparation of CdS quantum dot materials with increasingly improved optical properties. The Arizona group would test these materials, fabricate novel devices, and characterize them. Based on the test results, especially the values of the nonlinearity and emission properties of $\chi^{(3)}$, UCLA would be able to modify the processing method to yield even better samples. Simultaneously, samples of the desired sizes and shapes would be prepared and sent to Arizona for device fabrication and evaluation. Thus, a two-way feedback loop would be in place for the development of quantum dot waveguide devices. This unique collaboration would take advantage of the materials processing and fabrication expertise at UCLA and of the laser facilities and device development and fabrication expertise at Arizona.

Mackenzie, J.D.

A proposal entitled, "Development of Quantum Dot Materials for Optical Devices by the Sol-Gel Method" was submitted and approved in 1994 by AFOSR. During these past few years, in addition to the fabrication of CdS samples for the University of Arizona, the research efforts at UCLA have expanded to the preparation of CdTe and PbS quantum dot samples. Preliminary work has also been conducted in a new material which is a ferroelectric semiconductor, SbSI. The research performed at UCLA during the past three and one-half years is summarized in this Final Technical Report.

2. Research Accomplishments

A. Research on CdS Quantum Dot Glasses

High-quality CdS quantum dot (QD)-doped fully dense sodium borosilicate (NBS) glasses have been synthesized by the sol-gel process. Techniques of controlling QD size and size distribution have been developed: the use of a bifunctional ligand, 3-aminopropyltriethoxysilane (APTES), and the use of a matrix requiring lower temperature for densification into a pore-free glass (see Fig. 1). Using this processing, CdS QD gels and glasses of different sizes were fabricated and shown in Table 1.

The most significant finding was that very careful control of the heat-treatment time and temperature is necessary in order to obtain high quality CdS crystals. Figure 2 shows the crystallinity of the single crystals of CdS obtained. The need for careful heat-treatment is seen in Table 1 and in Figure 3 where the photoluminescence spectra clearly show that a temperature of 540°C for 6 hrs is necessary. The room temperature optical gain of a sample is shown in Figure 4. This is the first known result of optical gain at room temperature for a QD glass sample.

B. Waveguide Fabrication with CdS Samples

The sodium borosilicate glass matrix containing the CdS quantum dots is ideal for the Na for K ion exchange process to obtain a higher refractive index in selected portions of the glass. A process was successfully designed and

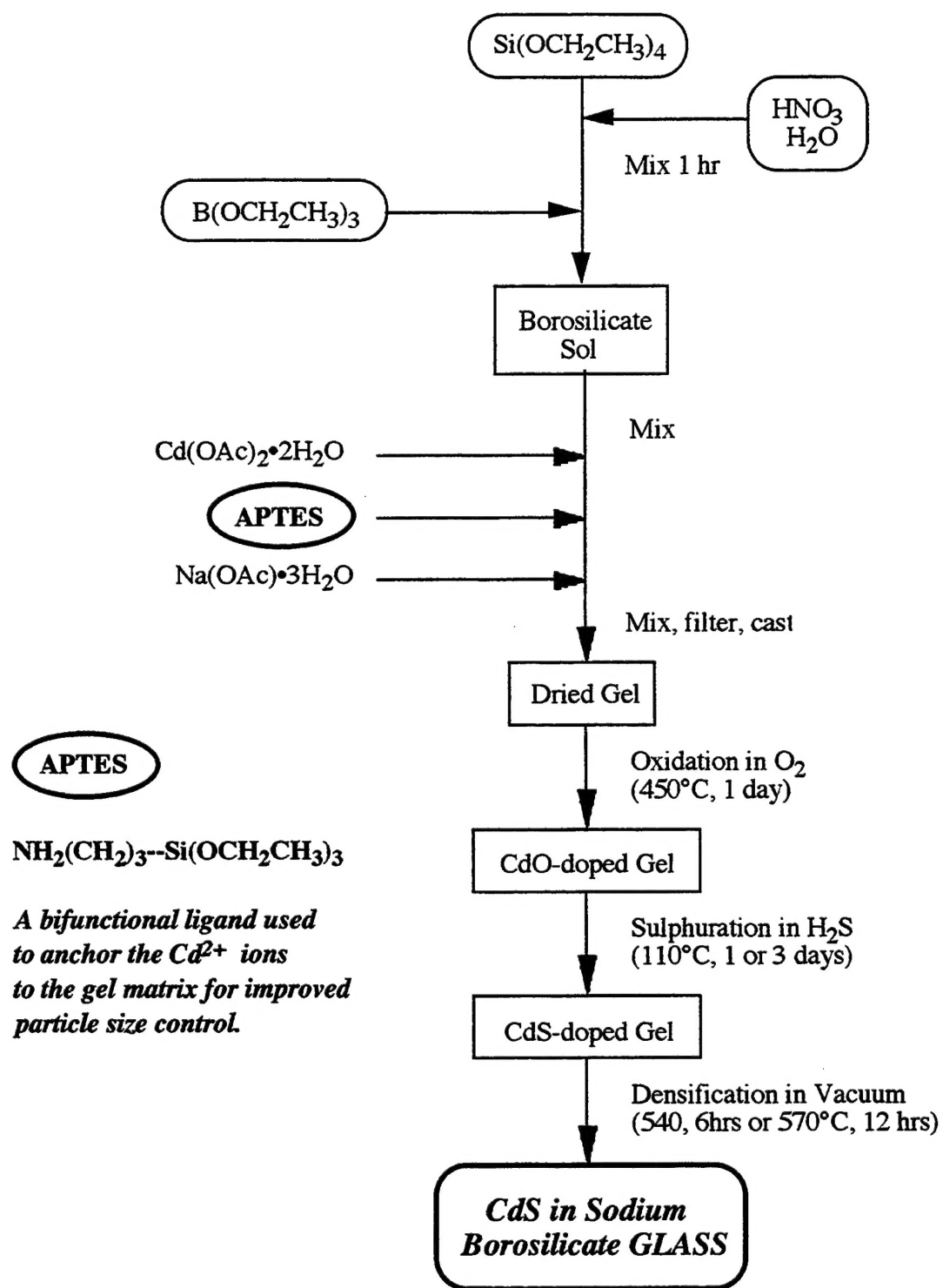
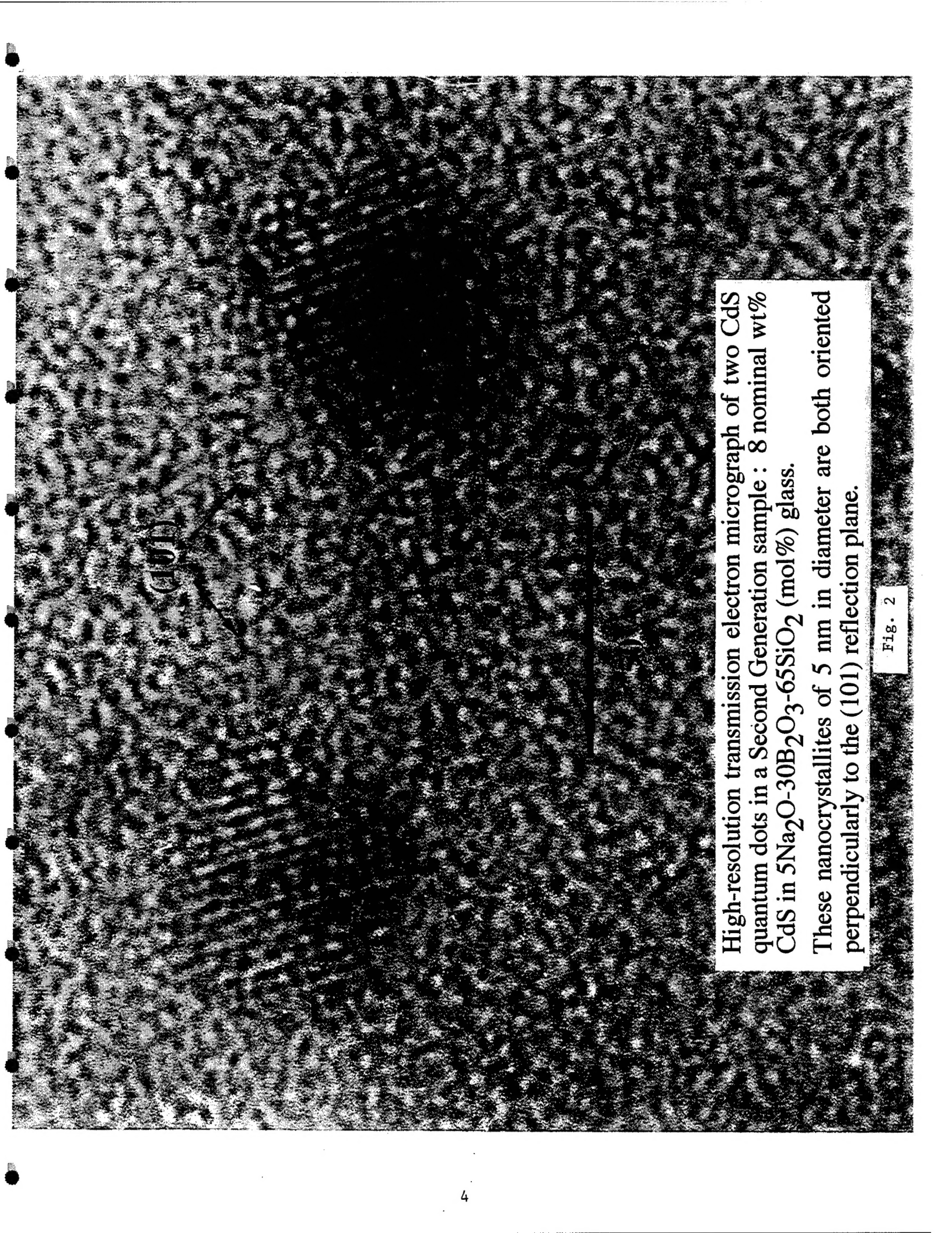


Fig. 1. Preparation of Second Generation CdS-doped sodium borosilicate glasses with controlled quantum dot size.



High-resolution transmission electron micrograph of two CdS quantum dots in a Second Generation sample : 8 nominal wt% CdS in 5Na₂O-30B₂O₃-65SiO₂ (mol%) glass. These nanocrystallites of 5 nm in diameter are both oriented perpendicularly to the (101) reflection plane.

Fig. 2

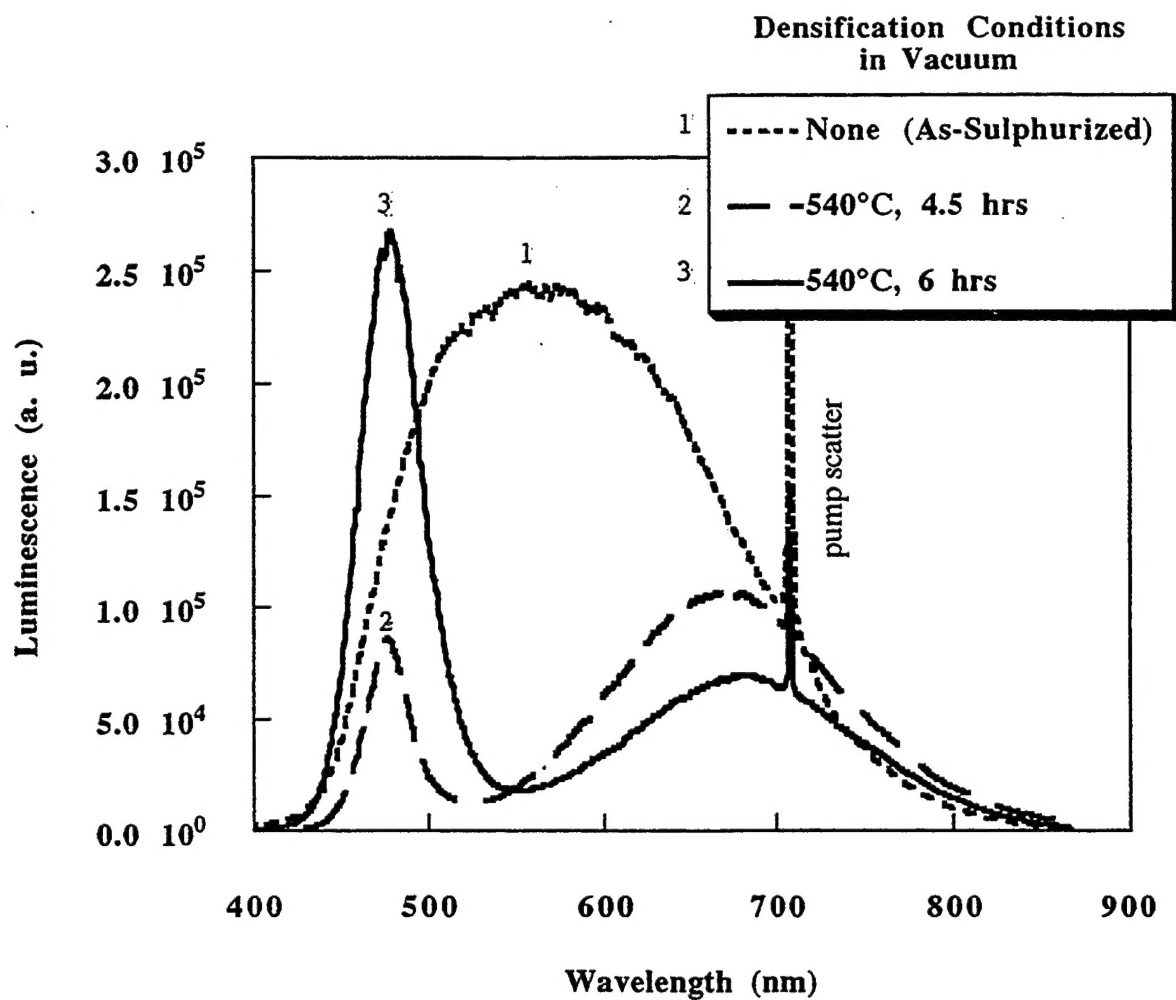


Fig. 3 Photoluminescence spectra of 8 nominal wt.% CdS quantum dots in 5Na₂O-30B₂O₃-65SiO₂ (mol.%) gel and glasses.
 $\lambda = 355$ nm, Intensity = 163 MW/cm², stripe length = 100 μ m.

Table 1
Samples with different CdS quantum dot sizes in NBS glasses

<i>Dot size and Processing Conditions</i>	<i>Gel* (No Gain)</i>	<i>Glass #1 (RT Gain)</i>	<i>Glass #2 (Gain)</i>	<i>Glass #3 (Gain)</i>
Confinement regime Average diameter (nm)	$r_{ave} \ll r_{Bohr}$ 2.7	$r_{ave} \ll r_{Bohr}$ 3.5	$r_{ave} < r_{Bohr}$ 3.9	$r_{ave} \sim r_{Bohr}$ 5.7
Standard deviation (nm)	0.7	0.7	0.9	2.0
Nominal CdS (wt.%) Matrix	8 30% B ₂ O ₃	8 30% B ₂ O ₃	9 30% B ₂ O ₃	8 15% B ₂ O ₃
APTES/Cd (mol)	2.0	2.0	2.0	2.0
Oxidation (O ₂)	450°C, 24 hrs	450°C, 24 hrs	450°C, 24 hrs	450°C, 24 hrs
Sulphuration (H ₂ S)	110°C, 3 days	110°C, 3 days	110°C, 3 days	110°C, 1 day
Densification	-----	540°C, 4.5 hrs	540°C, 6 hrs	590°C, 12 hrs
Porosity (%)	30	3	0	0

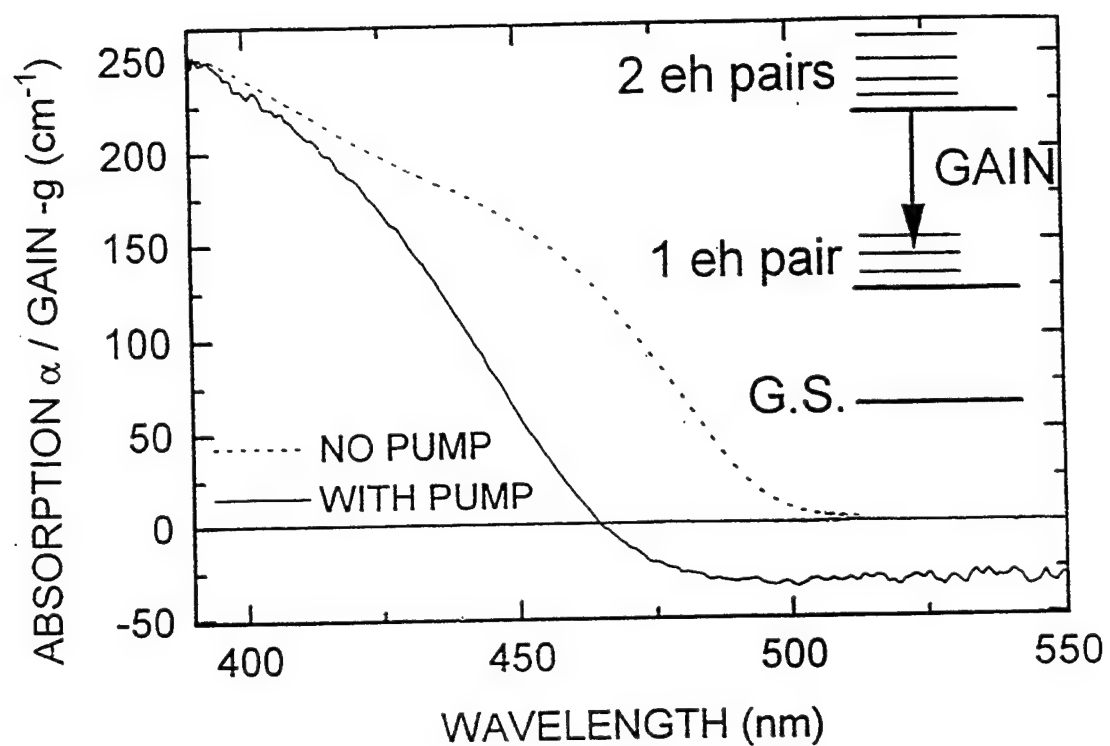


Fig. 4 Room-temperature optical gain spectra of a 8 wt.% CdS quantum dot-doped 5Na₂O-15B₂O₃-80SiO₂ (mol%) glass, measured in the pump and probe geometry.

$\lambda = 355 \text{ nm}$ $1 \sim 30 \text{ MW/cm}^2$, pulse duration = 5.5 ns.

carried out this past year using this technique to fabricate waveguides. The process is shown in details in Fig. 5. The completed waveguide is shown in Fig. 6 and light output from such waveguides are shown in Fig. 7. We have thus demonstrated that the CdS sodium borosilicate glass materials are potential candidates for the production of practical devices such as optical switches. This know-how and technique can be used to fabricate other quantum dot samples based on sodium borosilicate glasses.

C. Research on CdTe Quantum Dots

Because of the larger Bohr radius of 75\AA vs. that of 28\AA for CdS, cadmium telluride quantum dots should have superior nonlinear properties. That is summarized in Fig. 8. In addition, CdTe is transparent to longer wavelength compared to CdS. If one were to use the same matrix material such as a sodium borosilicate glass, then a comparison of the properties of CdS and CdTe will furnish insight into the role of the excessive surface areas of the crystallites as well as the influence of the matrix. In this past two years we have embarked on the development of two processes to prepare CdTe quantum dots. the reason why CdS samples were first fabricated was that the chemistry leading to the formation of CdS is much better known than that for CdTe. When CdS QD samples were successfully made, it became clear that semiconductors with higher Bohr radii such as CdTe and PbS should be tried. Two methods to prepare CdTe were developed. These are shown in Figs. 9 and 10. It was found that method B was more efficient. The transmission electron micrograph of a CdTe QD sample is shown in Fig. 11. As for CdS, single crystals of CdTe were formed and embedded in the sodium borosilicate glass matrix.

D. Research on PbS Quantum Dots

The Bohr radius of PbS is estimated to be 180\AA , even much larger than that of CdTe, PbS is also transparent to much longer wavelengths than CdS and CdTe, in fact to the near infrared. The larger Bohr radius should result in larger changes of the refractive index for the same laser intensity. Thus,

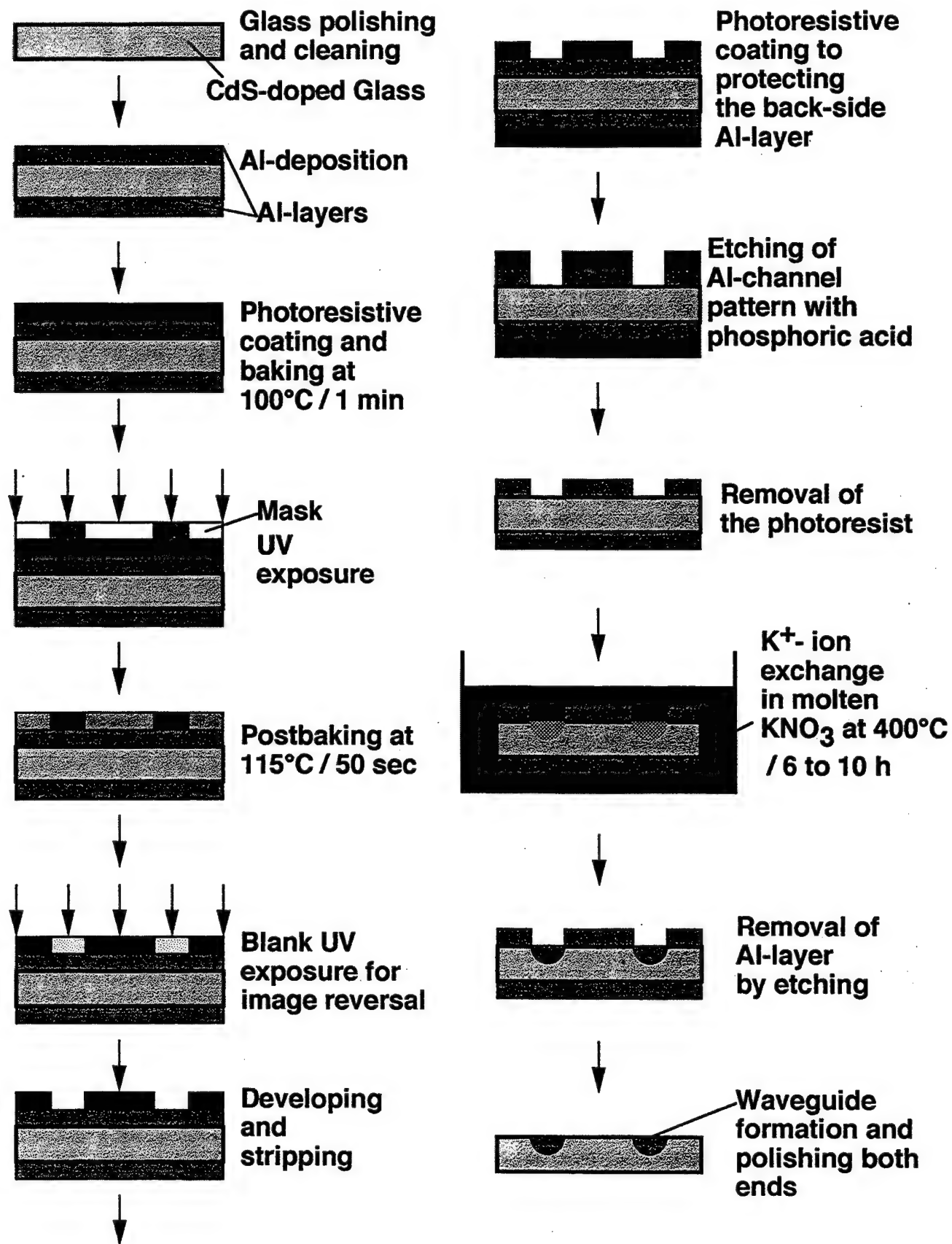


Figure 5 Processing for fabrication of an optical waveguide device

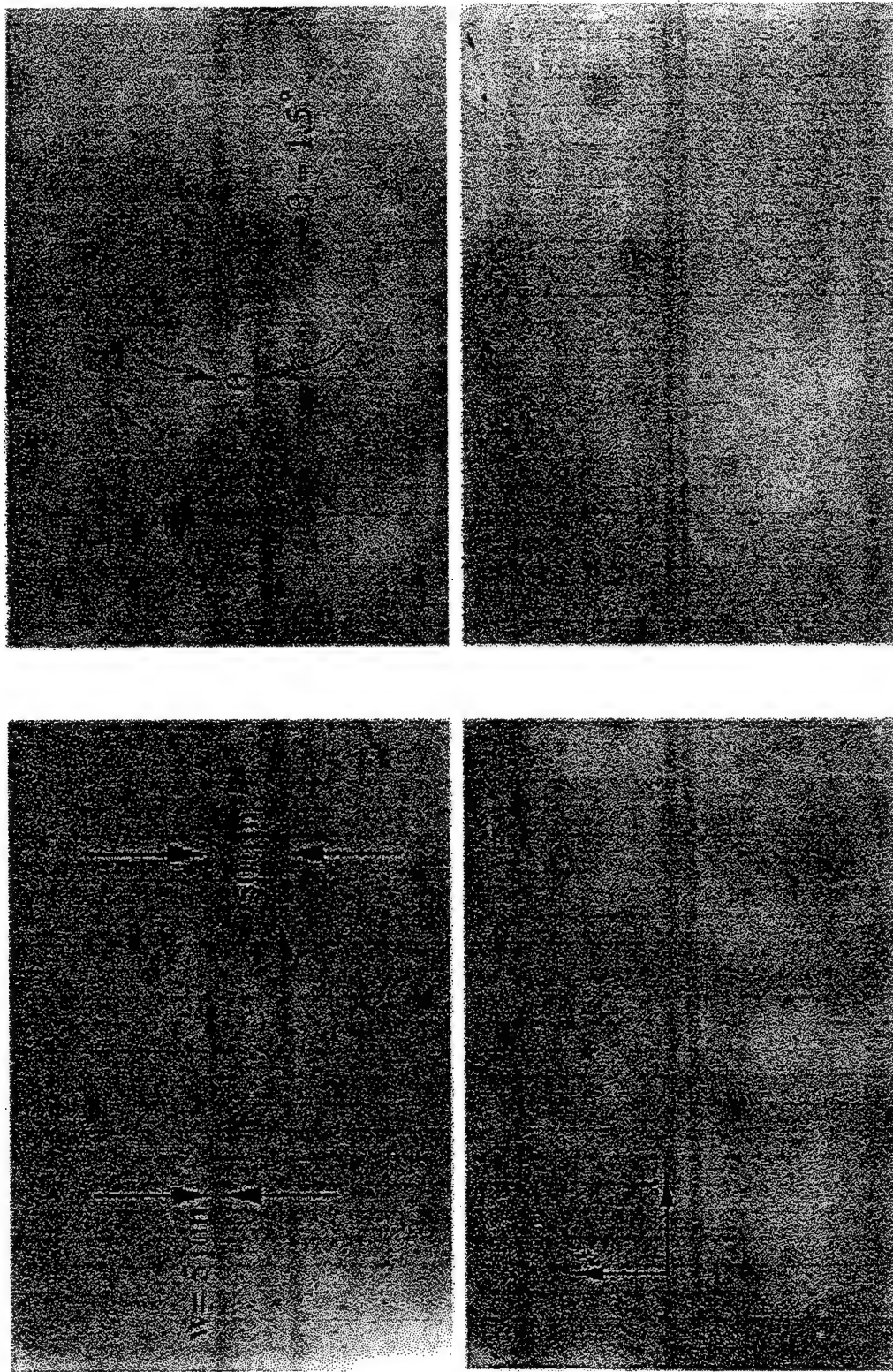
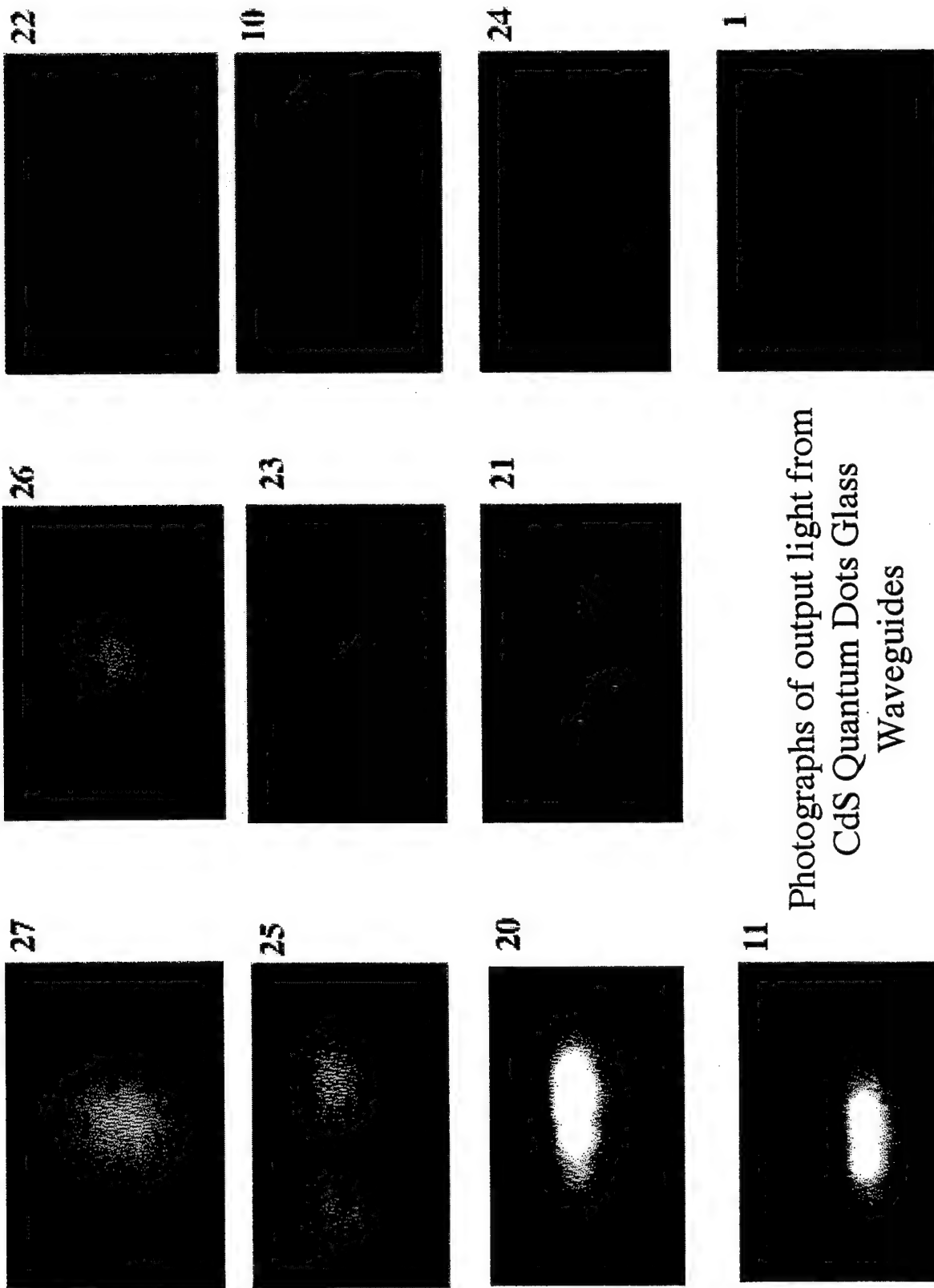


Fig. 6 Photograph of K⁺ ion-exchanged CdS Quantum Dots Glass Waveguide

Shape equation is $y = \frac{x}{40} + \sin 2\pi \left(\frac{50}{2\pi} \right) \sin 2\pi \left(\frac{x}{200} \right)$



Photographs of output light from
CdS Quantum Dots Glass
Waveguides

Fig. 7

Semiconductor	r_B (Å)	E_g (eV)
CdS	28	2.5
CdSe	53	1.7
CdTe	75	1.5
GaAs	124	1.4
PbS	180	0.41
New QD material (SbSI)	13000	2.0

$$\Delta n = \text{const.} \cdot (r_B/r)^3 \chi'(3) /$$

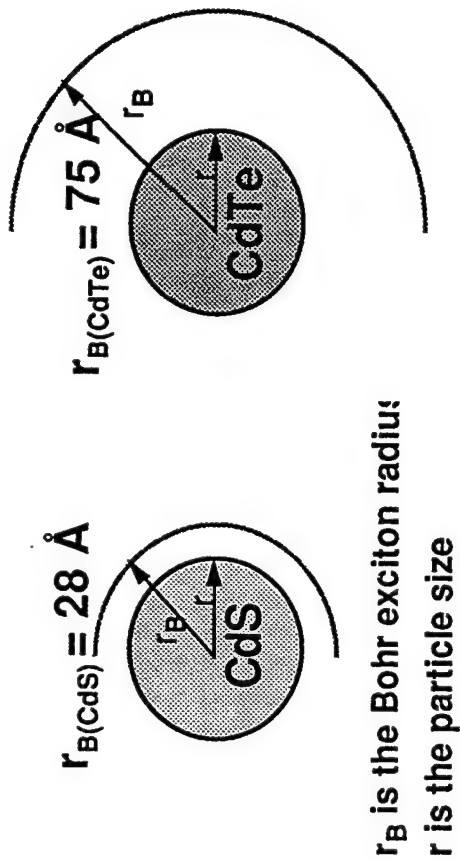


Fig. 8 Semiconductors and their bulk exciton Bohr radii, r_B , and energy gap, E_g

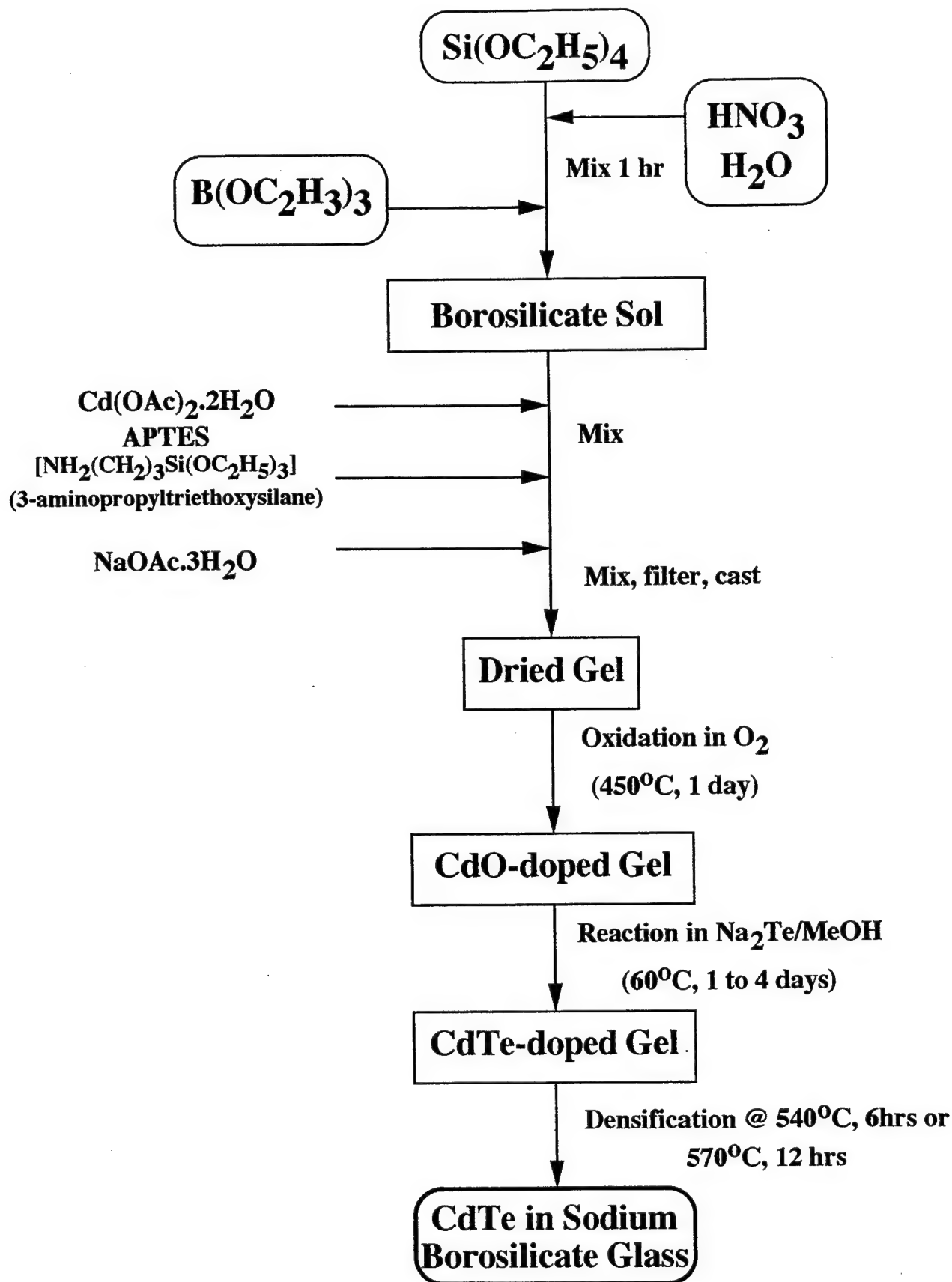


Fig. 9 Preparation of CdTe-doped Sodium Borosilicate Glass (A)

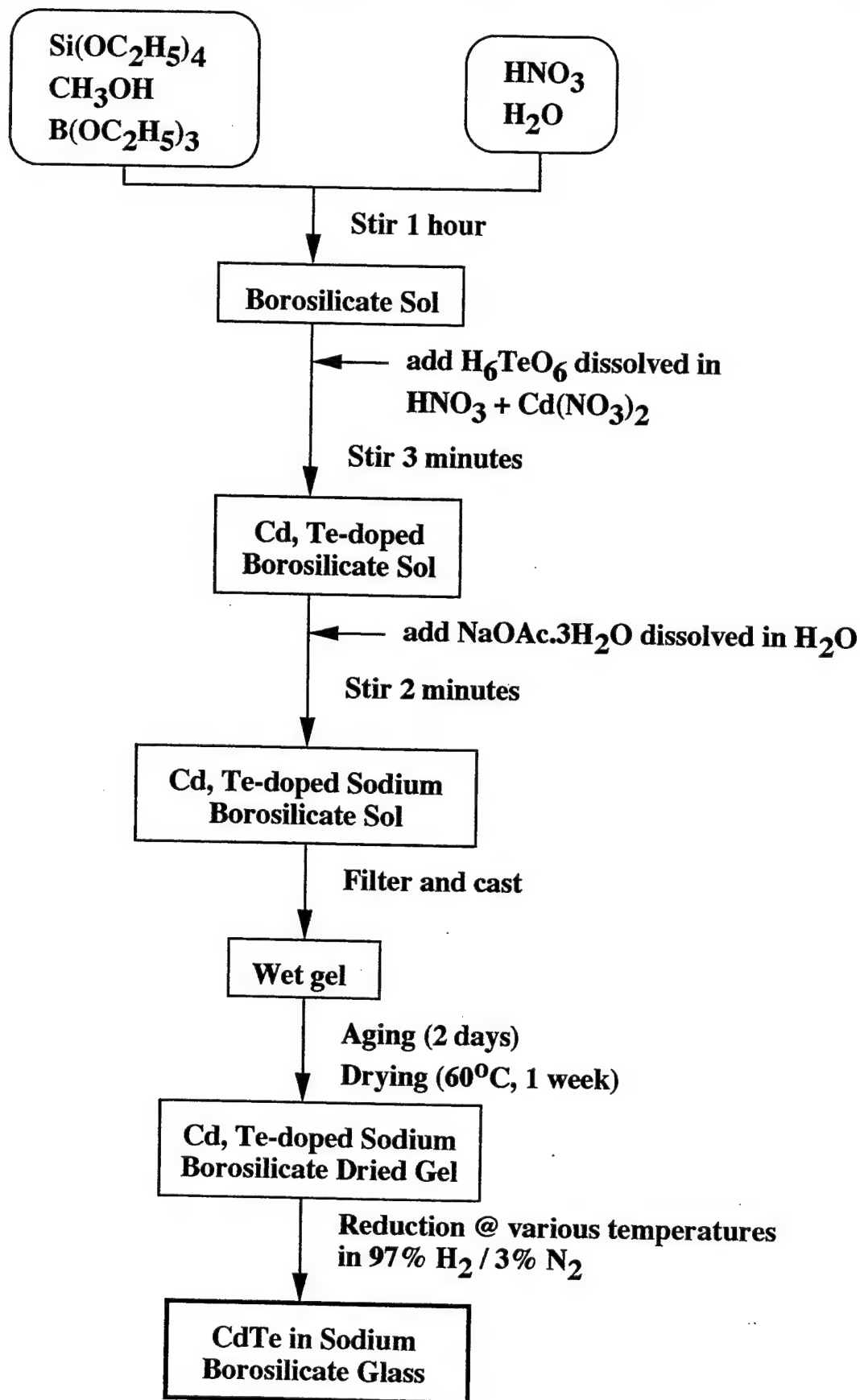


Fig. 10 Preparation of CdTe-doped Sodium Borosilicate Glass (B)

TEM of 10 wt% CdTe-doped glass heated to 520°C/4h

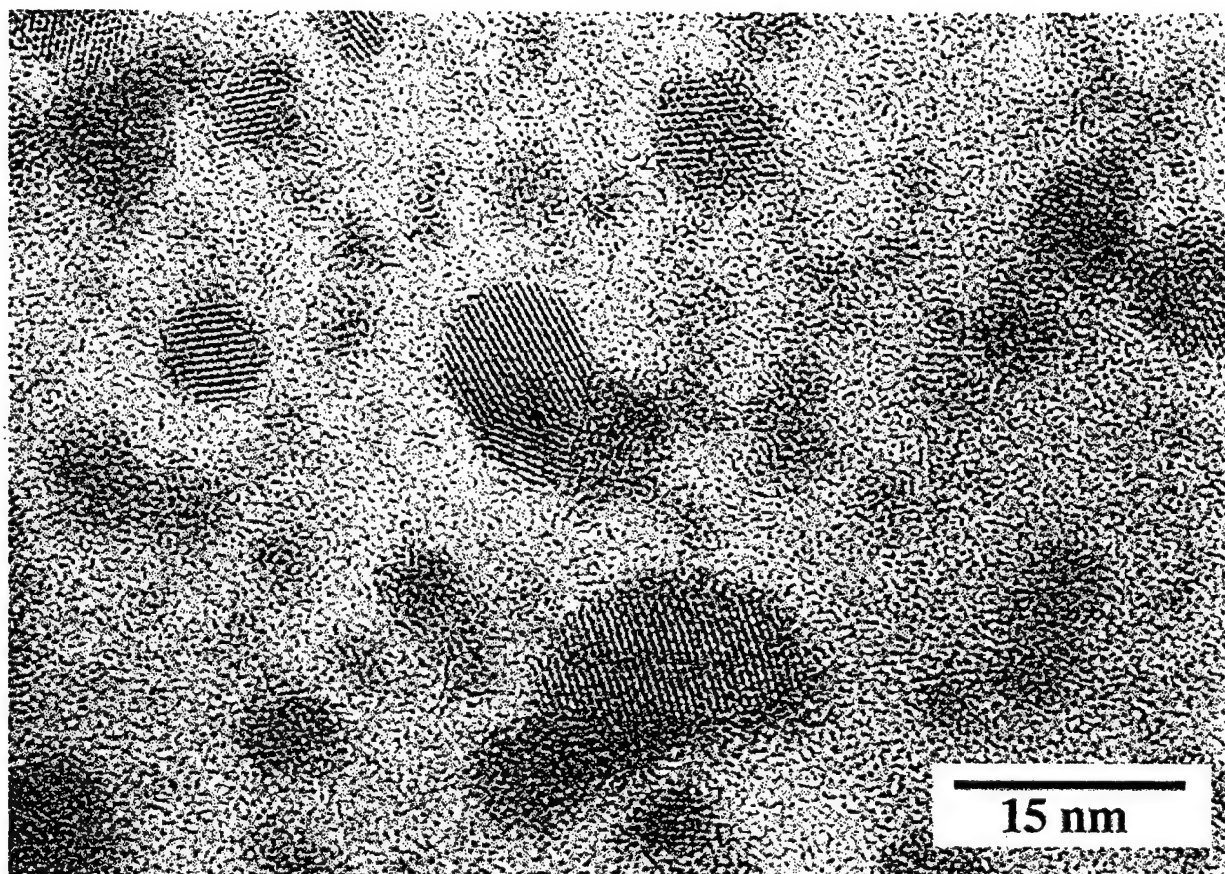
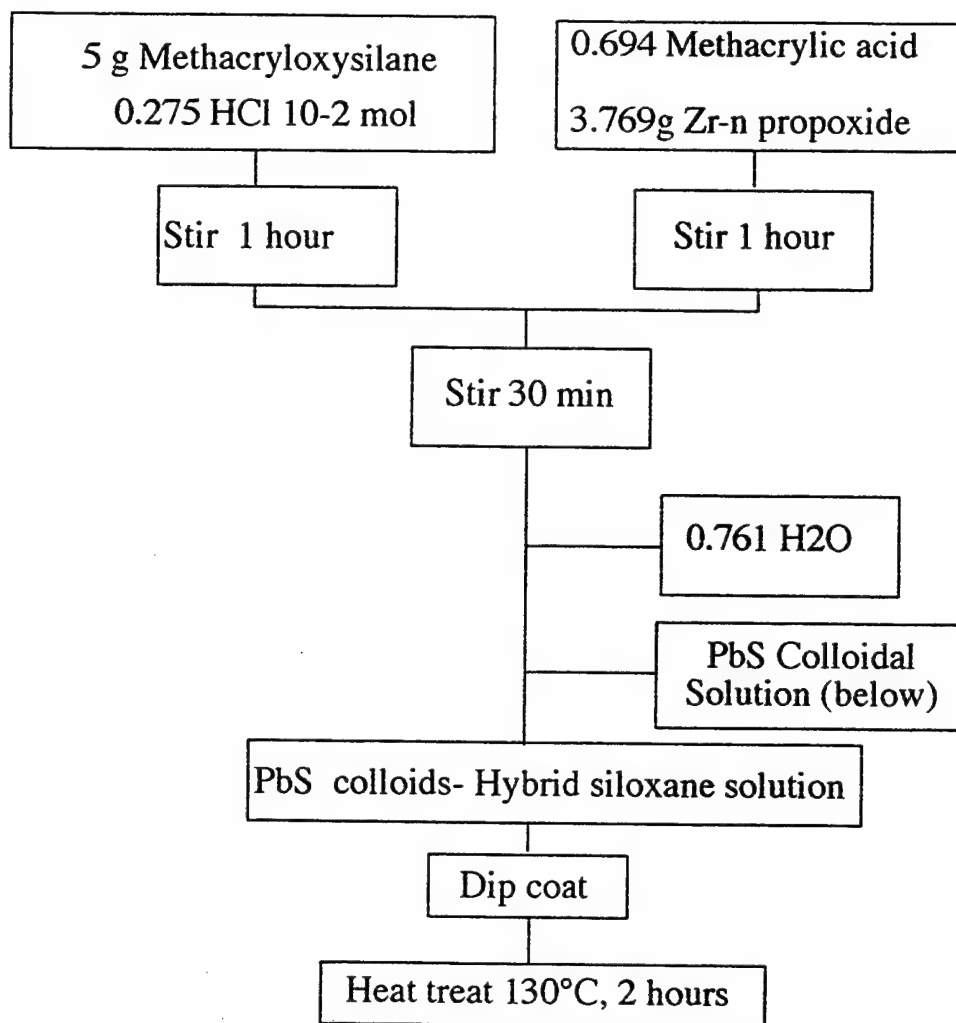


Figure 11

theoretically, PbS quantum dots are the most desirable of the three semiconductor materials being investigated under the present AFOSR grant. It has already been mentioned that despite the theory for quantum dots, the roles of the matrix and excessive surface area of the crystallites are presently not known. Further, it is also unknown if the control of dot size, size distribution, non-stoichiometry, matrix-semiconductor interactions, etc. are similar for all semiconductors. It is, therefore, necessary to study all three candidate materials. In the past two years a program has been agreed upon between UCLA and Tucson for collaboration on the two objectives of gaining scientific knowledge and the rapid fabrication of samples for device evaluation with PbS. It has been agreed that thick film waveguides made with PbS in Ormosils (organically modified silicates) and sodium borosilicate glasses on borosilicate glass substrates should be fabricated. The process to fabricate Ormosil thick film PbS samples is shown in Fig. 12. Initial experiments have been successful in the preparation of such samples as shown by X-ray diffraction. The high resolution electron microscopy results of such a sample are given in Fig. 13. Samples are now being prepared for Professor Peyghambarian's group for waveguide fabrication.

E. Research ON SbSI Quantum Dots

All known semiconductors being studied as QD candidates are covalent crystals. The application of an electric field on such crystals is not expected to result in the formation of permanent electric dipole. During the past year in a literature search we discovered that the compound SbSI is not only a semiconductor but is also a ferroelectric. This poses an interesting question as to the possibility of preparing an entirely new type of QD materials. In Fig. 8 it is seen that the Bohr radius of SbSI is enormous and thus it will be orders of magnitude superior to even PbS. In addition to the large Bohr radius, theoretically one can also exploit the ferroelectric behavior of SbSI. When a laser beam impinges on a crystal of SbSI, electron-hole pairs (excitons) are created. Most excitons will have a limited life-time before recombination.



PbS Colloidal solution

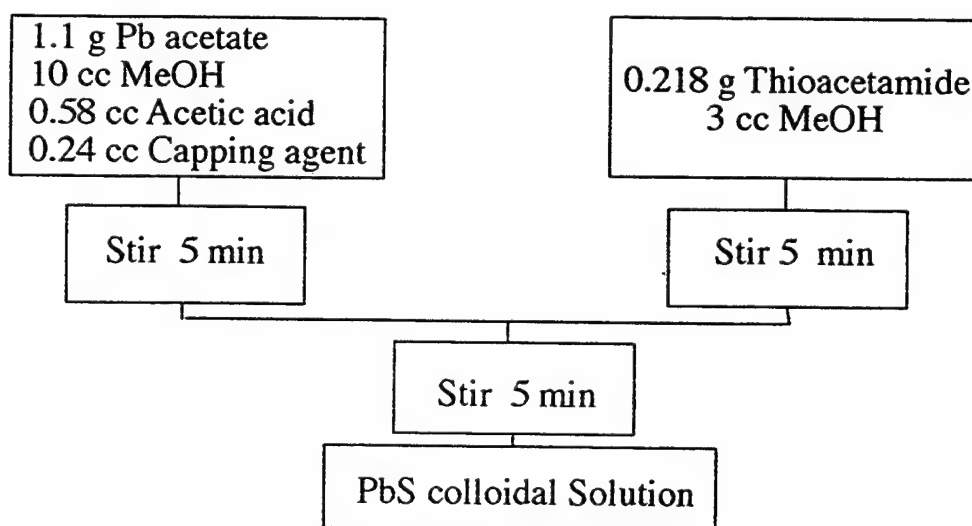


Fig. 12 Processing of PbS Quantum Dot-doped Ormosils

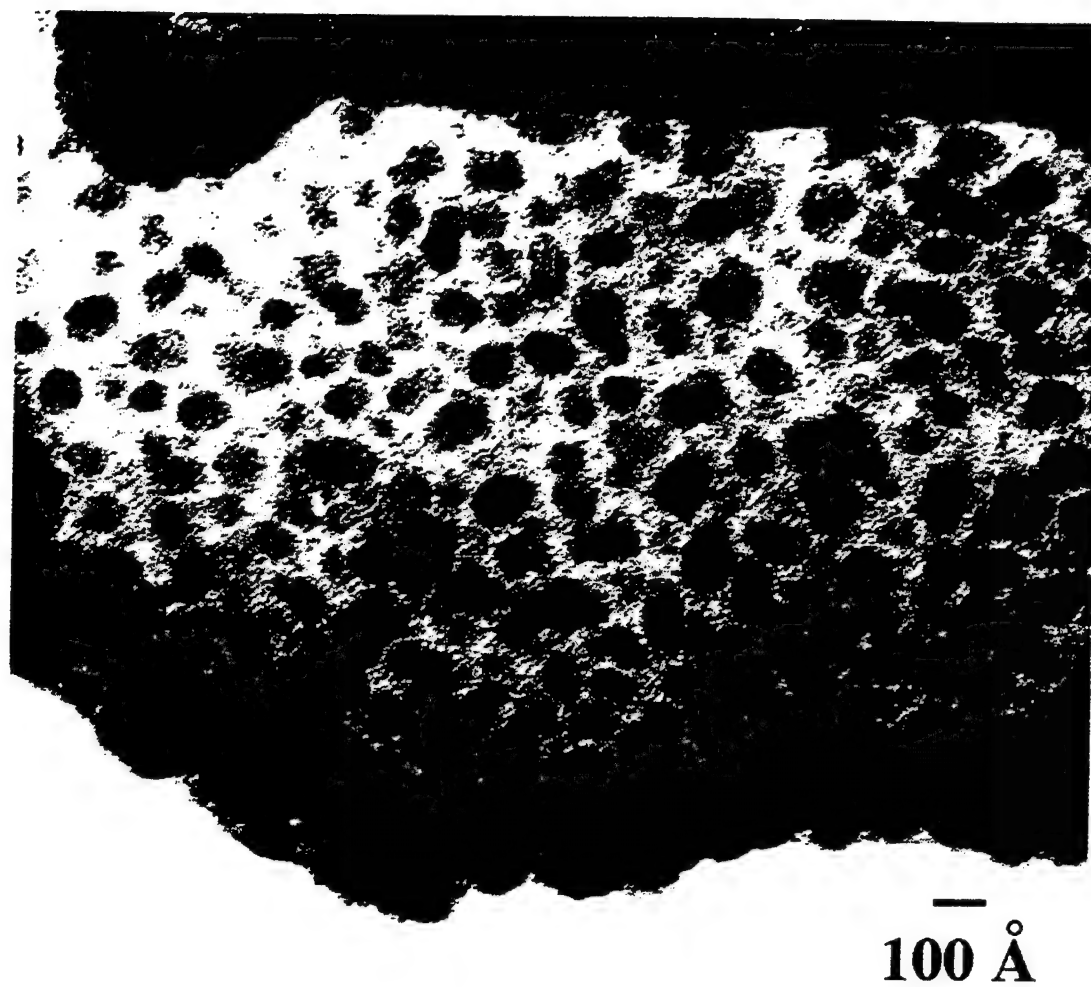


Fig. 13 PbS Quantum Dots in Sol-Gel Derived Matrix

However, if permanent dipoles are created when an electric field is also applied to SbSI, then it is reasonable to assume that the presence of electric dipoles will act to trap the electron-hole pair. A longer life-time is thus possible. This can be exploited for a variety of devices. A new optical delay line concept is presented in Fig. 14. We have recently developed a new method to fabricate SbSI QD samples based on the use of the sol-gel method as for CdS, CdTe and PbS. This exciting new concept remains to be tested. A proposal to continue with this research has been submitted to AFOSR and awaits approval.

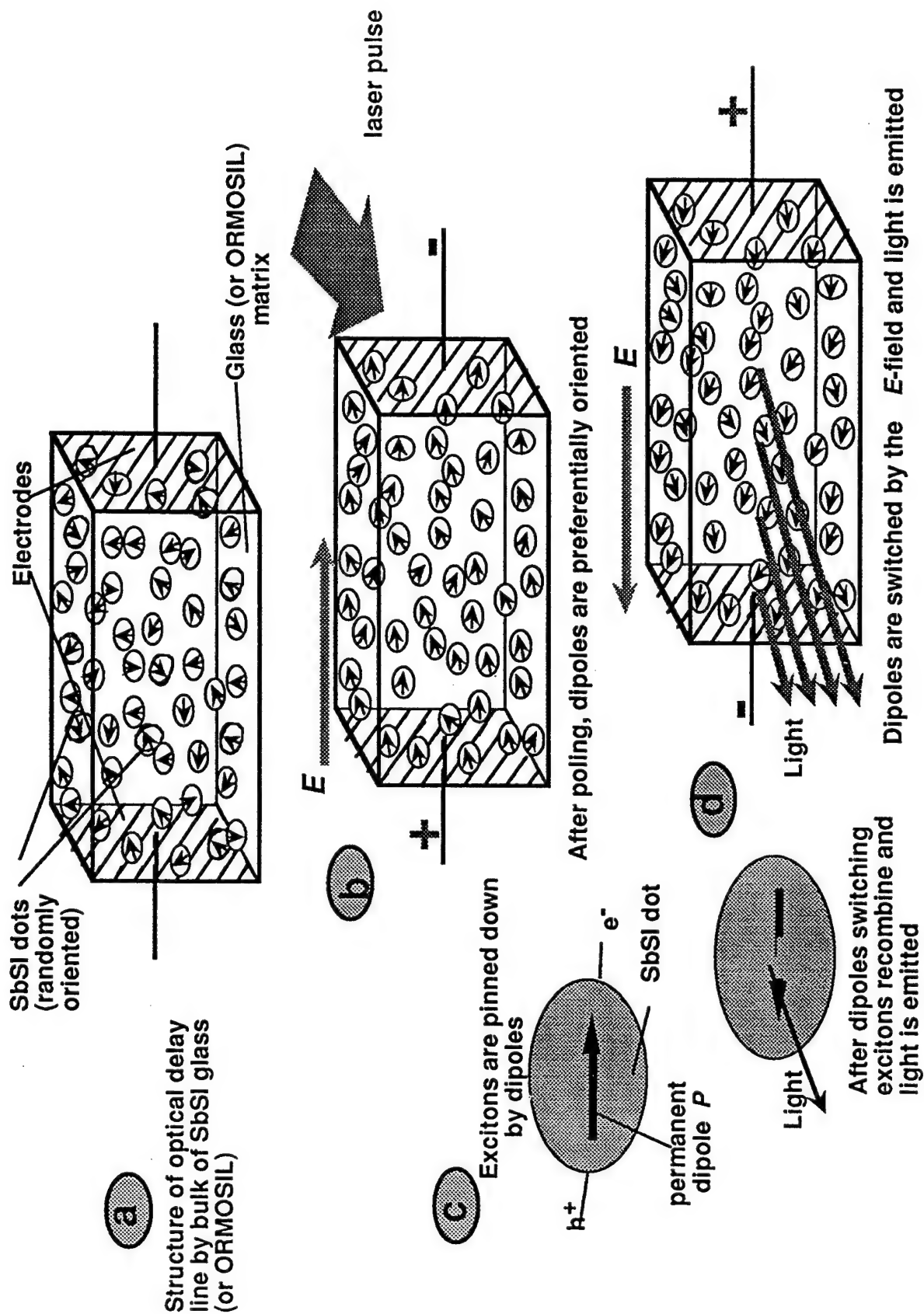


Fig. 14 New Optical Delay Line Device From SbSI QDs

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4. Personnel

During the duration of this research, the following people were supported by this grant:

Connie Chia	(M.S. student)
Justine Y. Tseng	(M.S. student)
Tammy Chau	(M.S. student)
Y. Hoshino	(Ph.D. student)
C-Y Li	(Ph.D. student)
Yuhuan Xu	(Ph.D. student)
Lisa Kao	(Ph.D. student)
Dr. Eric Bescher	(Postdoctoral Fellow, France)
Dr. I-C Ho	(Postdoctoral Fellow, Taiwan)
Dr. A. Matucci	(Postdoctoral Fellow, Italy)
Dr. F. del Monte	(Postdoctoral Fellow, Spain)

5. Professional Activities and Recognition

Professor J.D. Mackenzie was organizer and chair of Sol-Gel Optics III and IV in 1994 and 1997, respectively for the SPIE. These international conferences attracted audiences of 200-300 people and are now well-recognized by scientists and engineers involved in optical materials. Professor Mackenzie continues to be an active member of the International Advisory Committee, which organizes Workshops on Sol-Gel Science and Technology. The last two Workshops were in Portugal (1995) and in the United Kingdom (1997). Professor Mackenzie was named the Cecil and Ida Greene Honors Professor by Texas Christian University in 1994, the Samuel S. Scholes Lecturer by Alfred University, Alfred, New York in 1995 and the W.E.S. Turner Lecturer by Sheffield University, Sheffield, U.K. in 1996.